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13. ABSTRACT (Maximum 200 words) The research reported herein describes the first use of supercritical CO ₂ with solid state polymerization to produce high molecular weight polycarbonate. It was found that the increase in molecular weight is a strong function of CO ₂ pressure and temperature. Further, the solid state polymerization of polycarbonate in the presence of supercritical CO ₂ can be accomplished at temperatures as low as 90 °C. This suppresses side reactions that lead to colorbody formation and produces polycarbonate with excellent optical clarity and color. This synthesis can be scaled-up to industrial levels and could completely eliminate the use and production of toxic chemicals, significantly reduces the reaction temperature, and generates high-quality polycarbonate for use as transparent armor and numerous other commercial applications.			
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SYNTHESIS OF HIGH MOLECULAR WIEGHT POLYCARBONATES USING SUPERCRITICAL CO₂

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1. MOTIVATION AND RELEVANCE TO DOD

Transparent armor plays a critical role in soldier protection by combining a clear field of vision with ballistic protection. Key DoD uses include rotorcraft bubbles, visors, faceshields, goggles (including those for laser-eye protection), and portholes in armored vehicles. Poly(bisphenol A carbonate) is the polymeric material used by DoD for transparent armor due to its desirable properties, which include exceptional toughness, thermal stability, strength, and transparency. In addition polycarbonate is extensively utilized in the private sector in industries related to law enforcement, music, electronics, and in electrical, automotive and architectural applications. However, there is one critical drawback to polycarbonate use. Polycarbonate is prepared by an interfacial reaction between phosgene dissolved in methylene chloride and an aqueous alkaline solution of bisphenol A (Figure 1) (Schnell et al., 1962).

The result of this synthesis, which is used in the production of more than 2.7 billion pounds of polycarbonate per year, is the production and use of phosgene, a chemical so hazardous it was used as a chemical weapon in World War I. In addition the process generates hazardous aqueous and chlorinated organic waste streams that pose a significant threat to the environment resulting in expensive post-production treatment.

Prior to our research, a viable, environmentally benign approach to polycarbonate synthesis has never been proposed. Our research describes a new approach to polycarbonate synthesis that is solvent free and carried out in solid particles. This is accomplished by polymerizing low molecular weight polycarbonate beads without using solvents, and at very low temperatures, creating the possibility of significant energy savings for large-scale production.

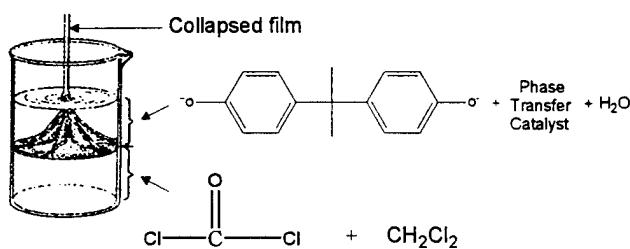


Figure 1. Commercial interfacial synthesis of polycarbonate using phosgene and methylene chloride.

2. RESEARCH BACKGROUND

Solid state polymerization is the method of choice by industry for step growth polymerizations. It is used in the manufacture of polyethylene terephthalate, PET, a large-scale step-growth polymer that is used for plastic soda bottles, milk bottles, and viewgraphs (a critical Army application), to name a few. In a solid state polymerization, a semicrystalline oligomer is heated between its glass transition temperature, T_g , and its melting temperature, T_m . At the same time a sweep fluid is passed over the surface of the particles to remove the condensate by-product driving the forward reaction to produce high molecular weight polymer particles. Prior to our research polycarbonate has not been prepared like PET because it does not

thermally crystallize. However polycarbonate can be made semicrystalline using supercritical CO_2 (Beckman et al., 1987). This has been used by our group as the basis for exploring a solvent-free, solid state polymerization for polycarbonate. Our research focuses on the synthesis of high molecular weight polycarbonate, defined as 25,000 - 40,000 g/mol weight average based on industry standards, using supercritical CO_2 for particle crystallization and by-product removal.

3. RESEARCH RESULTS

Initially bisphenol A and diphenyl carbonate were reacted in a melt condensation reaction to form low molecular weight prepolymer in the range 2,500 - 5,000 g/mol (Figure 2) (Gross et al., 1999). Low molecular weight prepolymer is used because it avoids problems caused by high viscosity and high reaction temperatures during chain extension reactions. The prepolymer was exposed to supercritical CO_2 at temperatures and pressures in the ranges 40 - 70 °C and 204 - 340 bar, depending on prepolymer molecular weight, to generate semicrystalline morphology. This is critical to prevent coalescence and melting during solid state polymerization. The semicrystalline prepolymer was heated between T_g and T_m while a sweep gas or fluid, N_2 or supercritical CO_2 , was flowed over the particles to remove phenol, the reaction by-product.

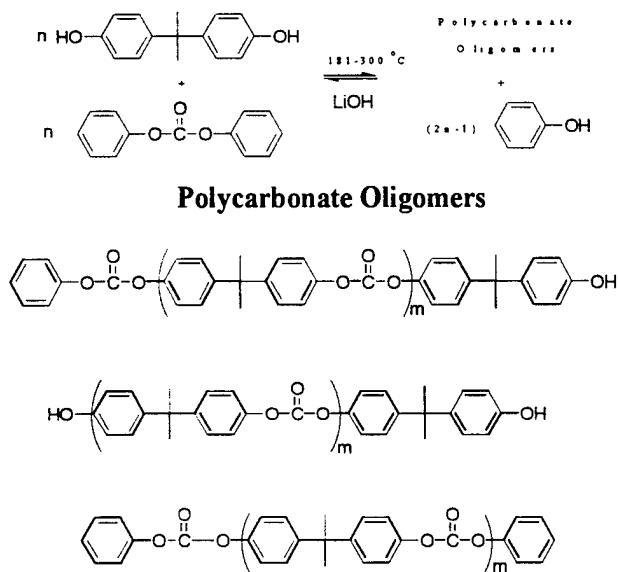


Figure 2. Melt condensation reaction of bisphenol A and diphenyl carbonate to form low molecular weight prepolymer.

Figure 3 shows the percent crystallinity as a function of time at 204 bar for a polycarbonate sample with a M_w of 1.8×10^4 g/mol, at different crystallization temperatures. The results show that a sample of intermediate molecular weight has a maximum induced crystallization of approximately 18%. A close inspection of the data reveals some interesting facts about the relationship between crystallinity and temperature.

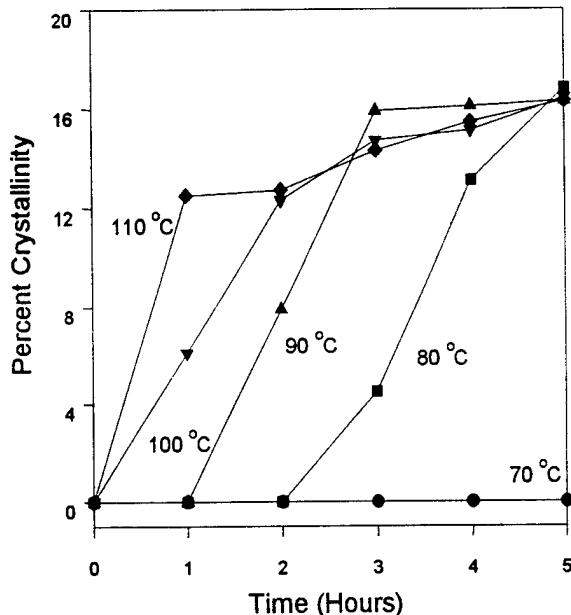


Figure 3. Percent crystallinity induced by supercritical CO_2 in poly(bisphenol A carbonate), $M_w = 1.8 \times 10^4$ g/mol, as a function of temperature at 204 bar.

At lower temperatures, it takes considerably longer to induce crystallinity than at higher temperatures. At 80 °C, 2 hours pass before crystallinity is detected by DSC measurements. However experiments run at 110 °C show that a significant degree of crystallinity is induced for this M_w sample relatively quickly. Therefore it appears that the nucleation period for crystallization decreases as the temperature of the crystallization experiment increases. It is also interesting to note that once crystallization is initiated for samples at any temperature, the maximum is rapidly approached and the crystallization rate drops off rapidly.

The M_w of polymer samples run at 160 °C and 180 °C are shown in Figure 4. Since it was observed that T_m increased during the polymerization, we also ran a polymerization where the temperature was raised

with time, i.e., 180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours and finally 240 °C for 6 hours. For the sample polymerized at 160 °C, the final M_w was 6.5×10^3 g/mol after 12 hours, while for the sample polymerized at 180 °C, the final M_w was 1.1×10^4 g/mol after the same time.

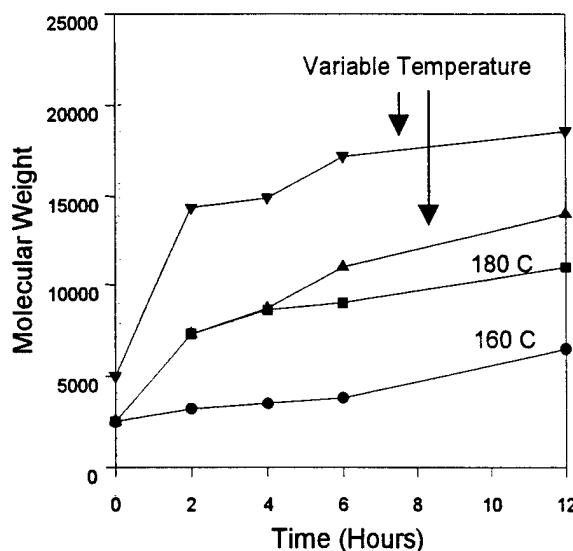


Figure 4. Increase in M_w of three samples of poly(bisphenol A carbonate) with a $M_w = 2,500$ g/mol from solid state polymerization at different temperatures over 12 hours. The increase in M_w of a sample initially 5,000 g/mol is also included. The time-temperature profile for the reaction was 180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours and 240 °C for 6 hours.

In a polymerization where the temperature was increased over time, the final M_w was 1.4×10^4 g/mol. The increase in molecular weight demonstrates that the use of supercritical CO_2 to induce crystallinity is compatible with the solid state polymerization of polycarbonates. Solid state polymerization was also carried out for prepolymer with a molecular weight of 5,000 g/mol using the same temperature-time profile. The results of this experiment exploring the effect of initial molecular weight on solid state polymerization under these reaction conditions are also shown in Figure 4. The results show that a modest increase in molecular weight at the start of the polymerization results in a significantly higher molecular weight.

As the polymerization proceeded, T_m increased significantly and the samples became progressively more crystalline. These results can be seen in Figures 5 and 6, respectively. For the sample polymerized at 160 °C, the final T_m and percent crystallinity were 225 °C and 32 percent after 12 hours, while for the sample

polymerized at 180 °C, the final T_m and percent crystallinity were 229 °C and 37 percent after the same amount of time. In the polymerization where the temperature was increased over time, the final T_m and percent crystallinity were 259 °C and 51 percent after 12 hours.

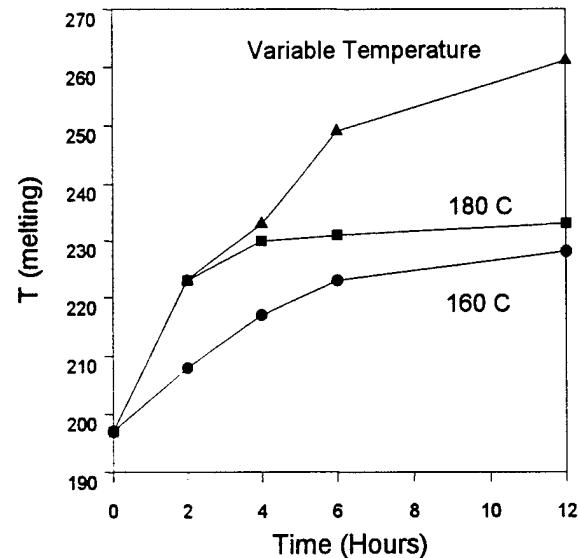


Figure 5. Increase in the T_m of poly(bisphenol A carbonate), $MW = 2,500$ g/mol, from solid state polymerization. The time-temperature profile for the reaction was 180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours and 240 °C for 6 hours.

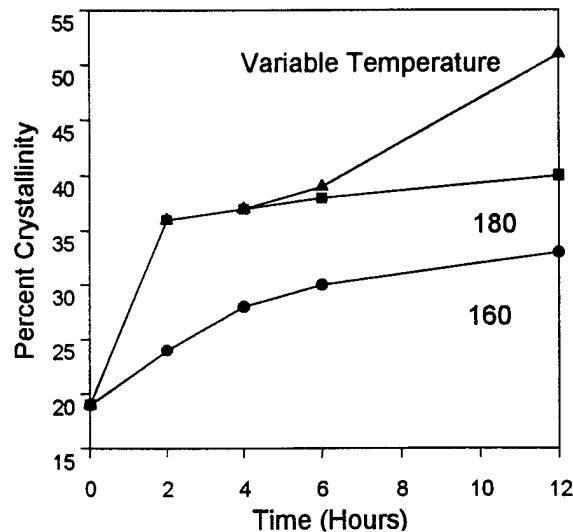


Figure 6. Increase in percent crystallinity of poly(bisphenol A carbonate), $MW = 2,500$ g/mol, from solid state polymerization. The time-temperature profile for the reaction was 180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours and 240 °C for 6 hours.

An increase in crystallinity with chain extension during solid state polymerization has been previously observed by Iyer et al., 1993 and Radhakrishnan, et. al., 1994. This phenomena was explained by the fact that the polymer was significantly reorganized in the solid phase, leading to the development of more perfect crystallites (Richardson et al., 1978)

The percent crystallinity and the molecular weight were determined as a function of time and radial position (defined as core = 0 - 0.4 mm, intermediate = 0.4 - 1.4 mm, and shell = 1.4 - 1.8 mm) for polycarbonate beads that were 3.6 mm in diameter (Gross et al., 2000). This is critical to understand in order to determine the optimum conditions for preparing high molecular weight polymer. The molecular weight and percent crystallinity (Figures 7 and 8) are strong functions of the particle radius due to the slow diffusion of phenol, the by-product of the polymerization, out of the polycarbonate beads.

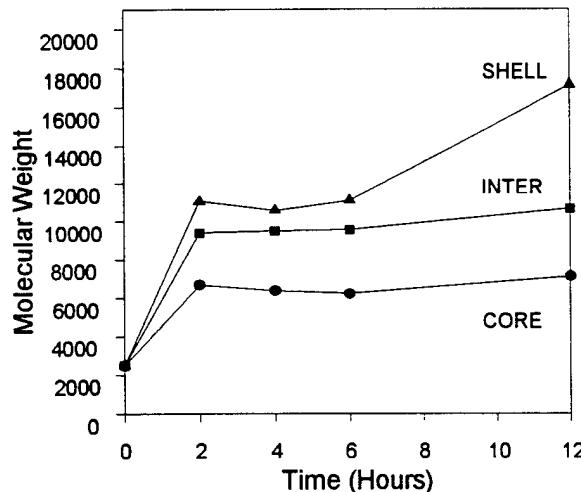


Figure 7. Weight average molecular weight for three regions of a polycarbonate bead with starting $M_w = 2,500$ g/mol for a solid state polymerization over 12 hours. The time-temperature profile for the reaction was 180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours, and 240 °C for 6 hours.

The result is a molecular weight gradient that ranges from 6000 g/mol in the core where phenol is trapped, to nearly 18,000 g/mol in the shell where phenol can readily escape due to contact with the sweep fluid. Molecular weight and crystallization gradient data are important results that demonstrate the role of prepolymer particle size in the solid state polymerization process. This dependence is not observed for melt phase polymerization, which industry uses to produce polycarbonate. The dependence of several parameters on particle size was

explored and it was determined that 20 μm diameter particles would eliminate effects due to particle size.

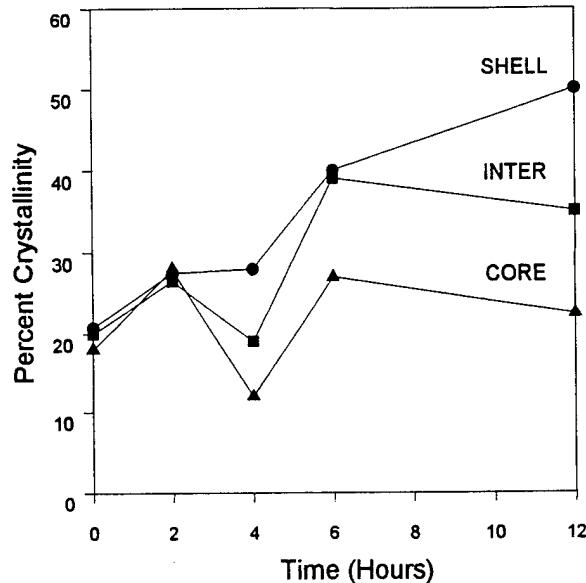


Figure 8. Percent crystallinity measurements for three regions of a polycarbonate bead initially 19% crystalline for a solid state polymerization over 12 hours. The time-temperature profile for the reaction was 180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours, and 240 °C for 6 hours.

T_m was also measured as a function of time for the 3 different regions of the particle (Figure 9). It was previously shown that the T_m increases as the molecular weight increases in the particle (Gross et al., 1999). It was found that the increase or decrease in T_m paralleled the increase or decrease in crystallinity in the different regions of the particle. Percent crystallinity and T_m measurements were made on beads that were not heated isothermally but rather from an experiment during which the temperature increased with time. This experimental condition leads to different morphological effects in different regions of the particle over time. For example, in Figure 8 the percent crystallinity decreases with time from 2 to 4 hours and from 6 to 12 hours in the core and intermediate regions of the particle. We speculate that the higher reaction temperatures melt the smaller imperfect crystallites in these regions reducing the level of crystallinity.

The gradient in crystallinity is not surprising when considering to the solid state polymerization induced crystallization observed in the experiment with nitrogen as the flow gas (Gross et al., 1999). Since the shell undergoes the greatest degree of polymerization, it follows that it is more crystalline

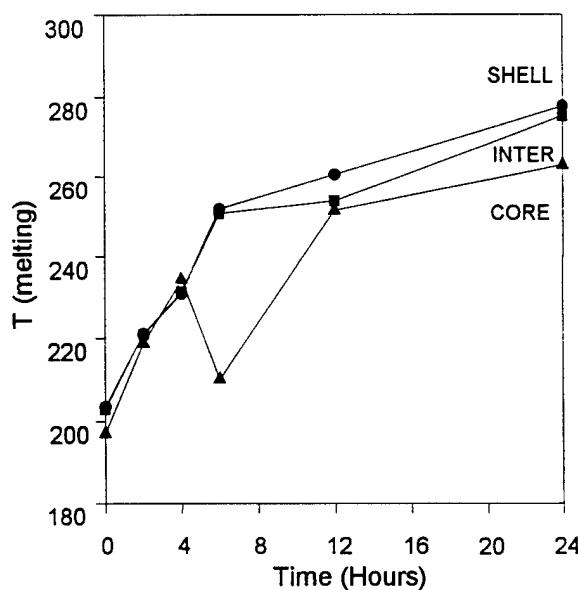


Figure 9. Melting temperatures for three regions of a polycarbonate bead initially 19 % crystalline from a solid state polymerization over 24 hours. The time-temperature profile for the reaction was 180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours, and 240 °C for 6 hours.

than the other regions. The increase in T_m with molecular weight is presumably due to the fact that more perfect crystallites are forming during the chain extension reactions. This is likely due to the greater number of crystallites with a less perfect structure in these regions than in the surface region of the particle. As the temperature is increased these less perfect crystallites melt in the interior regions.

In the previous work, the polymer beads had a significantly greater polydispersity index (PDI = M_w/M_n) than expected by theory. This broadening in molecular weight was likely due to the slow diffusion of phenol from the interior of the larger polymer particle. Locally the PDI was close to theoretical maximum of 2; however the overall particle exhibited a PDI of 2.6.

In Figure 10, the polydispersity index for polycarbonate beads and polycarbonate powder after solid state polymerization are compared as a function of time under similar reaction conditions. The polymerization temperature was increased over time (180 °C for 2 hours, 205 °C for 2 hours, 230 °C for 2 hours and 240 °C for 18 hours). The polydispersity of the powder remained just below 2.0 while the polydispersity of the bead was 2.6.

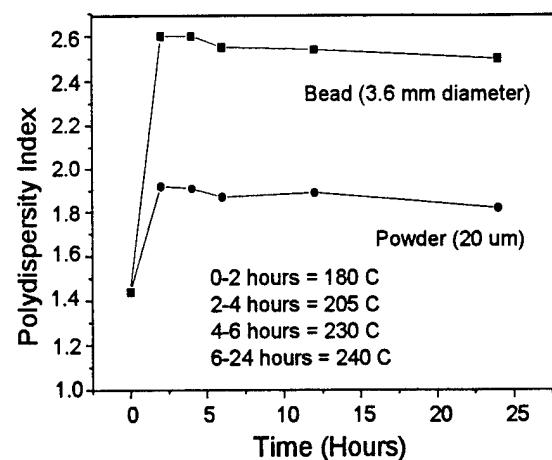


Figure 10. The polydispersity index, M_w/M_n , versus time for two different sized polycarbonate samples, 20 μm and 3.6 mm, following solid state polymerization. The time-temperature profile is noted. The sweep gas was nitrogen at a flow rate of 2 mL/min.

The use of supercritical CO_2 as a sweep fluid was explored because it plasticizes polycarbonate, potentially enhancing the reaction rate in the amorphous region. In addition phenol is highly soluble in supercritical CO_2 possibly facilitating a higher conversion through its efficient removal.

A range of CO_2 pressures was studied under isothermal conditions. As seen in Figure 11, a greater degree of polymerization results as the pressure increases in the presence of CO_2 at 120 °C. The increase in pressure probably accelerated the chain extension reactions for several reasons. Phenol should have a higher solubility in supercritical CO_2 at higher pressures under isothermal conditions (Hedrick et al., 1992). This should drive the reaction to a higher degree of polymerization. Additionally, the amorphous regions should be swollen to a greater degree as the pressure is increased. With this increase in free volume in the amorphous domains of the polymer, the endgroups should have a greater mobility, resulting in a greater rate for chain extension reactions. Also, the increase in free volume should allow the phenol to diffuse through a less entangled pathway in order to escape from the polymer particle.

Figure 12 shows the results of the solid state polymerization of 20 μm particles of poly(bisphenol A carbonate). The molecular weight is significantly higher for 20 μm particles, with $M_w = 36,000$ g/mol compared to $M_w = 18,000$ g/mol for 3.6 mm diameter beads for comparable conditions. In addition the

molecular weight distribution broadening observed in 3.6 mm diameter polycarbonate beads did not occur in 20 μm particles.

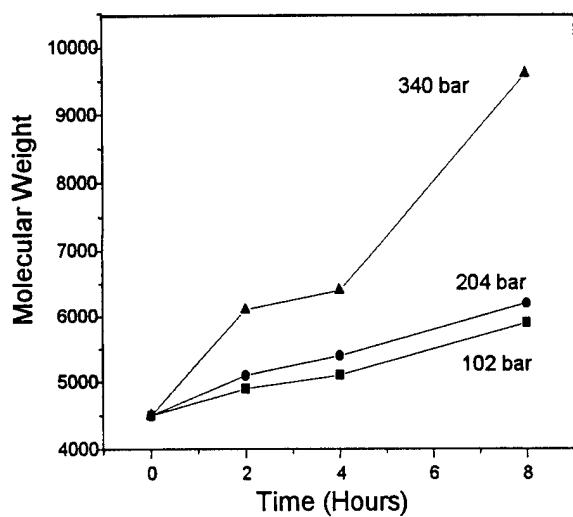


Figure 11. Increase in M_w for three samples of poly(bisphenol A carbonate). Initial $M_w = 4.5 \times 10^3 \text{ g/mol}$; particle size = 20 μm . Supercritical CO_2 was the sweep fluid at 102, 204 and 340 bar with a flow rate of 1 mL/min at 120 $^{\circ}\text{C}$.

The sweep gas is expected to facilitate the removal of the condensate by-product (phenol), thereby driving the forward reaction to high molecular weight polymer. N_2 is commonly used in industry, and it was used in this study at a variety of conditions as shown in Figure 12. We also used supercritical CO_2 as the sweep fluid, which is a novel approach. The polymerization rate was always higher in supercritical CO_2 at otherwise comparable conditions, and more significantly, the temperature of the reaction was in the range 90 - 120 $^{\circ}\text{C}$ when using supercritical CO_2 compared to 180 - 240 $^{\circ}\text{C}$ when using N_2 .

In order to achieve high molecular weight polycarbonate using N_2 , the temperature is ramped from 180 - 240 $^{\circ}\text{C}$ for up to 24 hours to compensate for changes in crystallinity and T_m as the polymerization progresses. When using supercritical CO_2 we propose that it plasticizes the amorphous regions of the polymer, thereby increasing chain mobility and the rate of phenol diffusion out of the polymer. This permits the reaction temperature to be reduced and also suppresses side reactions that lead to color body formation, which produces discolored polycarbonate.

By using supercritical CO_2 and a solid state polymerization, we have demonstrated the generation

of high molecular weight polycarbonate with excellent optical clarity using very low temperatures and without using any hazardous chemicals. We also note that the CO_2 used in these experiments was not produced for this research but was purchased as a by-product from other processes and is recycled.

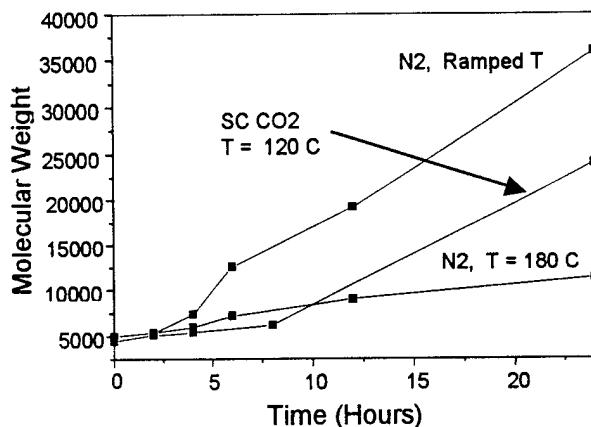


Figure 12. Increase in M_w for three polycarbonate beads for solid state polymerization under different reaction conditions. The N_2 flow rate is 2 mL/min. The time-temperature profile for the reaction was 180 $^{\circ}\text{C}$ for 0 - 2 hours, 205 $^{\circ}\text{C}$ for 2 - 4 hours, 230 $^{\circ}\text{C}$ for 4 - 6 hours, and 240 $^{\circ}\text{C}$ for 6 - 24 hours. The CO_2 flow rate is 1 mL/min and the pressure is 204 bar.

4. CONCLUSIONS

The research reported herein describes the first use of supercritical CO_2 with solid state polymerization to produce high molecular weight polycarbonate. It was found that the increase in molecular weight is a strong function of CO_2 pressure and temperature. Further, the solid state polymerization of polycarbonate in the presence of supercritical CO_2 can be accomplished at temperatures as low as 90 $^{\circ}\text{C}$. This suppresses side reactions that lead to colorbody formation and produces polycarbonate with excellent optical clarity and color. This synthesis can be scaled-up to industrial levels and could completely eliminate the use and production of toxic chemicals, significantly reduces the reaction temperature, and generates high-quality polycarbonate for use as transparent armor and numerous other commercial applications.

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PROVISIONAL PATENT

"Solid State Polymerization of High Molecular Weight Polycarbonate", Gross, S.M.; Roberts, G.W.; Kiserow, D.J.; DeSimone, J.M. submitted to the University of NC, Chapel Hill,

TECHNOLOGY TRANSFER

The results of this program are regularly discussed with S&Es at WMRD.

SCIENTIFIC PERSONELL ASSOCIATED WITH THIS PROGRAM

Stephen Gross, graduate student

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NOTEWORTHY AWARDS

Kiserow, Gross, Roberts, and DeSimone received a Scientific Achievement Award for the top paper in Materials Session at Army Science Conference, "The Elimination of Hazardous Chemicals in the Preparation of High Performance Transparent Armor for Soldier Protection".